Analysis of Phonon Heat Conductivity of Semiconductors

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Abstract

The various inadequacies of Callaway's phenomenological model of lattice thermal conductivity has been critically analyzed and the model is repaired in a modified form in which the systematic replacement of life time by line widths amicably resolves the various issues. The involvement of various scattering events in the heat transport, e.g., boundary scattering, impurity scattering, anharmonic phonon scattering, resonance scattering and interference scattering has been addressed in the new framework with the help of quantum dynamical many body theory. The technological importance of Ge is well known and hence it becomes significantto investigate the thermal behavior of it in details as its electrical properties are temperature dependent. Further, the CdTe also shows its vital importance in the fabrication of infrared optical windows and photo voltaic solar cells. The phonon heat conductivity of Ge and CdTe in the temperature range 3.3-298 K and 1.780-239.260 K based on the modified Callaway model have been analyzed and excellent agreements between theory and experiments are reported. The present formulation is found to be well justified and can be successfully applied for the calculations of thermal conductivity of several other crystalline solids.

Keywords

Lattice Thermal Conductivity; Phonons; Various Scattering

Introduction

Aconsiderable interest throughout the globe for more than a decade has been witnessed to develop the semiconductor based optoelectronic and nano technological devices. Of the widely used semiconductors Ge and Si, their unique physical properties like indirect band gap and large effective masses, the effort to develop mid infrared and fiber optic communication devices was limited (Wang K L, Cha D., 2007}, but some efforts have been pioneered to design low cost Ge-based photodetectors for near far infrared communication bands and high resolution spectral imaging (Wang J, Lee S., 2011).The modern low dimensional microelectronic devices on the same substrate such as quantum wells in the Si/Ge systems and Si/Ge and Si/Ge/C quantum dots have been tailored recently (Egorov V A, Cirlin G.. 2004). On the other hand, direct optical band gap (~1.5eV), III-VI compound semiconductor CdTe has been recognized as a very promising photovoltaic material to fabricate infrared optical windows (waveguides) (Rams J., Sochinskii N V., 2000) and solar cells (X Wu., 2004) and several applications has been developed in the field of nanotechnology as artificially tailored materials (Novoselov K S.and Castro A H., 2012). In semiconductors, the lattice thermal conductivity has been emerged as a fundamental transport property to facilitate the understanding of heat dissipation in the field of nanoelectronic and optoelectronic device fabrication with increased efficiency.

In the crystalline solids where most of the heat is transported by phonons, the theory of lattice thermal conductivity based on the Boltzmann transport equation approach via relaxation time approximation has sufferedfrom the commonshortcomings of kinetic theory (Peierls R., 1997). A more rigorous basis was acquired by the phonon transport theorywith the use of energy flux correlation techniques (Kubo R., 1957), however,these theories could not probe into successful numerical estimates. Of the various theories Callaway presented the most successful numerically amenable model to analyse thermal conductivity of non metallic solids. Following Callaway's theory, the expression for lattice thermal conductivity is given by (Callaway J., 1959).

$$K = (k_B T / 2\pi^2 v_p)(\beta\hbar)^2 \int_0^{\omega_D} \tau(\omega)\omega^4 e^{\beta\hbar\omega}(e^{\beta\hbar\omega} - 1)^{-2} d\omega \quad (1)$$

Where $v_p, \omega_D, \tau(\omega)$ stand for phonon velocity, Debye frequency, total relaxation time respectively and $\beta = (k_B T)^{-1}$ .In this model, Callaway made some assumptions, namely; (a) the phonon dispersion and anisotropy effects were ignored, thus the longitudinal

and transverse phonon modes behave identically, (b) the relaxation time has been considered as a function of frequency and temperature except boundary scattering relaxation time and (c) the relaxation times for different scattering mechanisms have been inversely added as $\tau^{-1}(\omega) = \sum_i \tau_i^{-1}$, where τ_i represents the relaxation time of the process 'i'. This greatly oversimplified model is, however, not complete and rigorous and leaves immense possibilities for modifications via above cited assumptions. In this context, Holland(Holland M G., 1963) made pioneering efforts in resolving Callaway expression of thermal conductivity into longitudinal and transverse components which werefurther refined by SDV model (Sharma P C, Dubey K S, and Verma G S., 1971), Tiwari model (Tiwari M D, and Agrawal B K., 1971) and others (Gairola R P., 1983, Bahuguna B P, Painuli C P and Indu B D.,1991). SDV and Tiwari-Agrawal models tried to repair the Holland model by including some generalized dispersion relations and found excellent agreements with experimental observations. Since the relaxation time $\tau(\omega, T)$ appearingin the heart of the problem has been worked out in many ways by several physicists (Pomeranchuk I., 1941, Klemens P G., 1965, Klemens P G., 1958, Erdos P, and Haley S B 1969) for a very long time, but in most of the treatments the frequent violation of Matthiessen's rule has beenobserved. In the modern approach (Gairola R P., 1983, Bahuguna B P, Painuli C P and Indu B D., 1991, Ansari M Ataullah, Ashokan V, Indu B D., 2012) the problem of evaluation of relaxation times has been taken up with the new perspectives in which the problem of exclusion of dispersion and violation of Matthiessen's rule has been amicably resolved.

In the present paper, these inadequacies have been overcomewith the help of quantum dynamical phonon Green's function theory (Gairola R P., 1983, Bahuguna B P, Painuli C P and Indu B D., 1991) in which the relaxation time hasbeen evaluated from phonon life time. On the basis of the new model, the thermal conductivities of Ge and CdTe has been analyzed and excellent agreements between theory and experimental data have been obtained in the following sections.

Theory

Owing to Matthiessen's rule, the relaxation times for various scattering events, namely; boundary scattering (τ_B^{-1}), impurity scattering (τ_D^{-1}), cubic and quartic phonon scattering $(\tau_{3ph}^{-1}, \tau_{4ph}^{-1})$,dislocation scattering (τ_{dis}^{-1}), resonance scattering (τ_R^{-1}), etc. can only be considered inversely additive if one considers them as independent (non-interacting) processes. However, it is not possible to consider their non interacting existence, because, there is sufficient possibility of interaction of these different collision processes. Contrary to this reality, we have come across to the most of the work which frequently violates the Matthiessen's rule. This problem can be resolved by making use of the relation between relaxation time τ and phonon frequency time width $\Gamma_k(\omega)$ as (Gairola R P., 1983, Bahuguna B P, Painuli C P and Indu B D., 1991, Ansari M Ataullah, Ashokan V, Indu B D., 2012, Indu B D., 1992).

$$\tau^{-1}(\omega) \approx \Gamma_k(\omega) + \tau_{CB}^{-1} + \tau_R^{-1} \quad (2)$$

Where the phonon line width $\Gamma_k(\omega)$ can be written as a sum of individual contributions to phonon line width coming from defects $\Gamma_k^D(\omega)$, cubic anharmonicities $\Gamma_k^{3A}(\omega)$, quartic anharmonicities $\Gamma_k^{4A}(\omega)$ and impurity-anharmonocity interactions $\Gamma_k^{AD}(\omega)$ in the form

$$\Gamma_k(\omega) = \Gamma_k^D(\omega) + \Gamma_k^{3A}(\omega) + \Gamma_k^{4A}(\omega) + \Gamma_k^{AD}(\omega) + \tau_{CB}^{-1} + \tau_R^{-1} \quad (3)$$

This treatment suggests the two fold modifications in Callaway model, namely; (i) the problem of violation of Matthiessen's rule is resolved through phonon line width concept, and (ii) $\Gamma_k(\omega)$ itself describes the details of frequency spectrum hence the inadequacy of exclusion of phonon dispersion has been overcome.

The boundary scattering relaxation time $\tau_B^{-1} = v_p / L$ ($L \equiv$ Casimir's length, which has been used as a parameter without any physical justification) can be modified by considering the involvement of crystal microboundaries and micro scale fluctuations in the form $\tau_B^{-1} = v_p / L(B)$ where $L(B)$ the modified Casimir's length includes the effects of microboundaries(Indu B D., 1980, Ansari M Ataullah, Singh Nitin P, Indu B D., 2007).

The phonon line width $\Gamma_k(\omega)$ has been evaluated with the help of double time thermodynamic Green's function theory via an almost complete Hamiltonian

which comprises the effects of defects, anharmonicities (Gairola R P., 1983, Bahuguna B P, Painuli C P and Indu B D., 1991, Ansari M Ataullah, Ashokan V, Indu B D., 2012, Indu B D., 1992) and the various components can given by

$$\Gamma_k^D(\omega) = 8\pi\varepsilon(\omega)\sum_{k_1} R(-k,k_1)R^*(-k,k_1)\omega_{k_1}\delta(\omega^2-\tilde{\omega}_{k_1}^2)$$

$$\approx A_1\omega^4 + A_2\omega^2 \quad (4)$$

Here A_1 and A_2 describe the mass change and force constant parameters, respectively which provide additional information as compared to Klemen's results containing the effects of mass change only (Klemens P G.,1958). The importance of this new term cannot be easily ignored because a very small change in central or noncentral force constants drastically changes the specific heat of a crystal [note that the specific heat term is an inevitable component of lattice thermal conductivity expression;

$$K = \frac{3}{(2\pi)^3}\int v^2\cos^2(\theta)\alpha(k)C_{ph}(k)d^3k\,.$$

Since the number of excited phonons continuously increases with gradually rising temperature towards LTC maximum, the probability of phonon-phonon scattering becomes comparable to defect scattering.If adequate information about the specimen as required in the first part of this equation is available, one can make parameter free calculations specially in case of tailored materials.Also

$$R(k_1,k_2) = (\omega_{k_2}/\omega_{k_1})C(k_1,k_2) + D(k_1,k_2) + 4\sum_{k_2} C(-k_1,k_2')D(-k_2',k_2)\omega_k^{-1} \quad (5)$$

The study of the effects of phonon-phonon and quartic phonon scattering has been a matter of long debate and the frequency and temperature dependent nature of these processes have been varied at the will of the workers and remained unjustified(Callaway J., 1959, Holland M G., 1963, Pomeranchuk I., 1941, Klemns P G., 1965, Klemns P G., 1958, Erdos P, and Haley S B., 1969). In the present work, this has been sorted out(Gairola R P., 1983, Bahuguna B P, Painuli C P and Indu B D., 1991, Ansari M Ataullah, Ashokan V, Indu B D., 2012, Indu B D., 1992) to give

$$\Gamma_k^{3A}(\omega) = \lambda V\omega_k^2\theta(\omega_L-\omega_k)/16\pi N\beta\hbar a_0 v^2 \approx B\omega^2 T \quad (6)$$

$$\Gamma_k^{4A}(\omega) = (\hbar/48M)(a_0\hbar\eta\varphi^{IV}V/4\pi^2\beta\varphi^{II}v^3)^2 \times(\tilde{\omega}_k^2+\tilde{\omega}_{k_1}^2-\tilde{\omega}_{k+k_1}^2) \approx B_H\omega^2T^2 \quad (7)$$

where λ is the dimensionless quantity and $\omega_k = \omega_L\sin(\pi k a_0)$ which shows the exact frequency and temperature dependence. The various symbols appearing in the above equations are obtainable in the form (Indu B D., 1992) and

$$S_{\pm\alpha} = n_{k_2} \pm n_{k_1} \quad (8)$$

$$S_{\pm\beta} = 1 \pm n_{k_1}n_{k_2} + n_{k_2}n_{k_3} \pm n_{k_3}n_{k_1} \quad (9)$$

$$\omega_{\pm\alpha} = \tilde{\omega}_{k_1} \pm \tilde{\omega}_{k_2}\,;\quad \omega_{\pm\beta} = \tilde{\omega}_{k_1} \pm \tilde{\omega}_{k_2} \pm \tilde{\omega}_{k_3} \quad (10)$$

$$\eta_{i-1} = \frac{\omega_{k_1}\omega_{k_2}.....\omega_{k_i}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}.....\tilde{\omega}_{k_i}}\,;\ n_k = \frac{\tilde{\omega}_k}{\omega_k}\coth\frac{\beta\hbar\tilde{\omega}_k}{2} \quad (11)$$

All of the above results are based on non-perturbative approach.

When the phonons of anharmonic fields enter the localized fields and interact with the phonons of impurity field, the impurity anharmonicity interaction modes occur which can be recognized by the line widths

$$\Gamma_k^{3D}(\omega) = (3\lambda V\mu_{-2}/\pi\beta\hbar a_0)[(M_0^2c(1-c)/4N\mu V)^2]\omega_k^4 \approx D\omega^4T \quad (12)$$

$$\Gamma_k^{4D}(\omega) = (3\hbar\mu_{-2}/MN)[(M_0^2a_0\hbar\varphi^{IV}V/16\pi^2\beta\varphi^{II}v^3\mu)^2 \times c(1-c)]\tilde{\omega}_k^4 \approx D'\omega^4T^2 \quad (13)$$

$$\tau_k^{-1} = \tau_{CB}^{-1} + A_1\omega^4 + A_2\omega^2 + (B+B_1e^{-\theta/aT})\omega^2T + D\omega^4T + \tau_R^{-1} \quad (14)$$

It is wise to note here that the processes related to quartic anharmonic interactions, e.g., $\Gamma_k^{4A}(\omega), \Gamma_k^{4D}(\omega)$ contribute tohigh temperatures and will not be included in the present study.

The presence of bump or dip in the thermal conductivity curve can be explained by a typical resonance phenomenoncharacterized by the relaxation time (Pohl R O., 1962, Walker C T, and Pohl R O., 1963)

$$\tau_R^{-1} = \frac{R\omega^2T^n}{(\omega_0^2-\omega^2)^2 + (\Omega/\pi)^2\omega^2\omega_0^2} \quad (15)$$

where R is a proportionality constant containing the concentration of impurities causing the resonant scattreing, ω_0 is the resonance frequency, and Ω describes damping of the resonance.

Analysis of Thermal Conductivity

For the purpose of analysis, we have taken the experimental values of the work of Hamilton-Parrott

and Holland (Hamilton R A H, and Parrott J E., 1969, Holland M G., 1964). For the sample of Ge, the observations are available in the temperature range (3.3-298K) and those for CdTe are reported in the range (1.780-239.260K). Due to the lack of sufficient information about the samples, we have taken some of the quantities in the analysis as reasonably justified(Gairola R P., 1983, Bahuguna B P, Painuli C P and Indu B D., 1991) parameters which are furnished as Table [1]. It is observed that at low temperatures, below the maximum thermal conductivity due to the excitation of low frequency phonons, the major contribution to thermal conductivity comes from the combined boundary scattering. As the temperature starts readily to rise, phonons of relatively higher frequencies get excited and start interacting with point impurities present in the specimen giving rise to defecting scattering phenomenon. Owing to gradual rise in temperature nearmaximum of the thermal conductivity curve the higher frequency phonons become available, which, in turn, invokes the phonon-phonon scattering processes. At the same time the phonons present in the anharmonic fields start interacting with localized phonon fields of point impurities giving rise to impurity-anharmonicity interaction modes. Thus the phonon-phonon scattering processes and interference scattering dominate in the close vicinity of the thermal conductivitymaximum and above.

Electrically inactive monoatomic impurities also give rise to the resonance scattering in the close vicinity of ω_0 which are also found to be very important in the present samples and capable to provide the best fit at the dip in the conductivity curve. The present calculations depicted in the figures [1] and [2] show an excellent agreement with experiments.

TABLE 1CONSTANTS AND PARAMETERS

Sample	Ge	CdTe
L(B) [cm]	0.146429	0.0861
$A_1 \times 10^{-44}\,[S^3]$	0.022	0.110
$A_2 \times 10^{-23}\,[S]$	20.734	--------
$B \times 10^{-23}\,[SK^{-1}]$	499.09911	598.09911
$B_1 \times 10^{-23}\,[SK^{-1}]$	53.85572	--------
$D \times 10^{-44}[S^3K^{-1}]$	1.062	6.689
$R \times 10^{30}\,[c/s]$	1.421	22.998
$\omega_0 \times 10^{12}[c/s]$	6.05551	5.32350
$\Omega\ \ [c/s]$	1.79	0.41
$a[cm]$	0.9798	--------
$v[cms^{-1}]$	3.11×10^5	3.11×10^5
$\theta_D[K]$	118	252

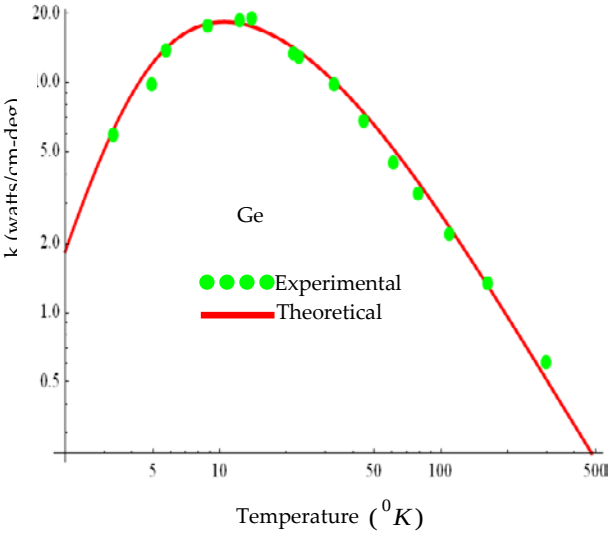

FIG. 1 ANALYSIS OF THERMAL CONDUCTIVITY OF Ge SAMPLE

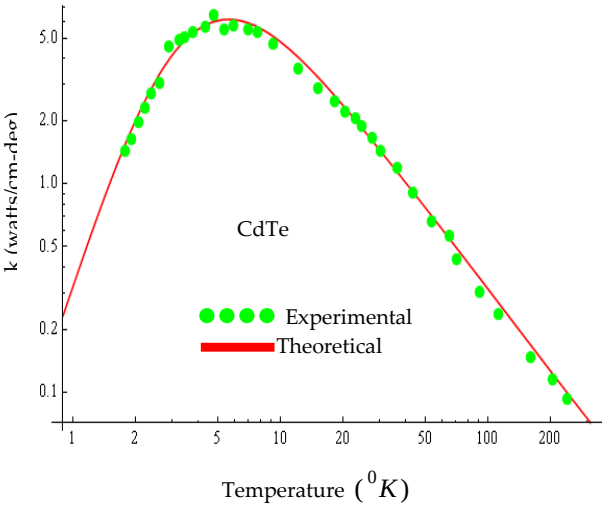

FIG. 2 ANALYSIS OF THERMAL CONDUCTIVITY OF CdTe SAMPLE

Conclusions

It can be statedfrom the present study that the various inadequacies left in the Callaway model havebeen almost removed by the quantum mechanical treatment of the phonon line widths. This modified model successfully explains the experimental observations of thermal conductivity and can be applied for the calculations of thermal conductivity of several other optoelectronic materials including artificially tailored low dimensional solids.

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